Validity of the BCS model Hamiltonian in the limit of small sizes

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(Received 8 May 2000)

Finite-size effects when the electronic level spacings become comparable to the bulk superconducting gap can suppress pairing correlations in small metallic particles. We examine an alternative mechanism for finite-size suppression of superconductivity: the role of the nonpair portion of the interaction, which could become important in small systems. We show that the crossover size at which the nonpair contribution becomes significant is typically already within the regime wherein finite level spacing suppresses the pairing correlations; however, the nonpair terms could become relevant in certain weak-coupled superconductors.

In sufficiently large systems at low temperatures energetic arguments will often favor simple correlations: the less restrictive the correlation, the greater the scope to superpose a large number of correlated states into an energetically favorable ground state. Examples can be found in both classical and quantum systems, e.g., the existence of crystalline periodicity in sufficiently large clusters and the irrelevance of fourfold and higher correlations in bulk BCS paired superconductors.[1] However, in sufficiently small systems, the phase space available for exploiting a simple energetically favorable correlation is more restricted and the situation can change qualitatively. A classical example here would be the nontetrahedral structures of small silicon clusters[2] (this point of view is more general and abstract than is one based on, e.g., the relative importance of surface and volume energies in such clusters).

In some cases, additional finite-size effects can arise from the discretization of energy levels, e.g., Anderson's observation that superconductivity is suppressed when the energy level spacing in a finite-sized superconductor exceeds the bulk superconducting gap.[3,4] More recent work has built from this observation to develop the interesting field of finite-size (and fixed-N) superconductivity, including studies of systems with equally spaced levels,[5] Wigner-Dyson level spacings,[6] fluctuation effects,[7] and fixed-N canonical treatments.[8] In these systems, the suppression of simple pair correlations through finite size is mediated by the coarsening of the level spacing. Here we consider an alternative mechanism which is independent of the existence of finite level spacings and can also limit the size at which pairing correlations take hold, namely, the size dependence of the nonpair correlated part of the interaction. This channel falls outside of the usual BCS model Hamiltonian, but could become important in sufficiently small systems wherein the phase space to exploit the pairing correlations is severely limited. A classical analog is again very small atomic (e.g., Si) clusters which assume structures that differ greatly from the local structure of the bulk crystalline lattice due to the inability to repeat the favorable structural motifs of the bulk system.

Although the nonpair-correlated part of the BCS one-square-well interaction oscillates randomly in sign,[9] these nonpair matrix elements comprise the vast majority of the Hamiltonian matrix. For sufficiently small systems the lowest eigenvalue of the random portion of the interaction matrix might be lower in energy than the BCS state, raising the question of when this crossover occurs. In a bulk system the BCS ground state is lower in energy than the normal state by roughly $N(0)\Delta^2 \sim N(\Delta/E_F)\Delta$ (N being the total number of electrons), a constant energetic lowering per electron.[10] The nonpair-correlated part of the Hamiltonian matrix contains a total number of relevant basis states $\binom{\tilde{N}}{\tilde{N}/2}$, where $\tilde{N} \equiv 2N(0)\hbar\omega_{\text{phonon}}$ gives the number of states which are active in superconductivity [and $N(0)$ has units of $(\text{energy})^{-1}$, not $(\text{energy volume})^{-1}$]. We concentrate on the interaction portion of the Hamiltonian instead of the kinetic component since we are interested in the rough size of the change in the energy upon introduction of the interaction.

The majority of the matrix elements between the basis states are zero, since the phonon mediated BCS electron-electron interaction connects states which differ in occupation numbers for only four electronic states. Fixing attention on a given initial many-electron state, the number of final many-electron states which give nonzero matrix elements is determined by first choosing two particular filled single-particle states as the electrons which will scatter in the initial many-particle state and then choosing one empty single-particle state in the initial many-electron state as a state into which an electron is scattered. The second empty state is determined by momentum conservation; the condition that it be empty introduces an inconsequential factor of one half. Picking these single-particle states from the vicinity of the Fermi energy, the fraction of nonzero matrix elements in the matrix representing the interaction is then essentially

$$\frac{\binom{\tilde{N}/2}{2}\binom{\tilde{N}/2}{1}}{\binom{\tilde{N}}{\tilde{N}/2}}. \tag{1}$$

Each nonzero matrix element is assumed to have a characteristic size $(1/N)\tilde{V}$, where $\tilde{V}$ is a volume-independent measure of the coupling matrix element.[11] $\tilde{V}$ might be reduced from the value in the pair-correlated channel due to the detailed character of the overlap integrals entering the matrix elements for short-ranged interactions,[3] but such a reduction is not necessary for the current argument.

Assuming no hidden structure in the matrix element distribution, the lowest eigenvalue of the essentially randomly signed uncorrelated piece of the interaction matrix can be estimated from random matrix theory. The matrix is the superposition of two distributions. One is a delta function at zero. The second can be approximated by a Gaussian distribution with standard deviation $(1/N)\tilde{V}$, where the results are insensitive to the exact form of this distribution. For calculational purposes the delta function can be approximated by a very thin rectangular distribution so that we superpose two distributions that both yield circle distributions of eigenvalues.[12] The result is then another circle distibution with lowest eigenvalue $\sqrt{M}\sigma$, where σ is the standard deviation of the entire distribution and M is the number of rows or columns in the matrix. The standard deviation is greatly reduced from $(1/N)\tilde{V}$ by the majority zero matrix elements, yielding a lowest eigenvalue

$$\frac{\tilde{V}}{N}\sqrt{\binom{\tilde{N}}{2}\binom{\tilde{N}}{1}} = \tilde{V}\frac{\tilde{N}}{N}\sqrt{\frac{1}{2}(\tilde{N}-1)} \tag{2}$$

which scales with system size[13] as $\sqrt{\tilde{N}}$ with rough value $\tilde{V}(\hbar\omega_{\text{phonon}}/E_F)\sqrt{\tilde{N}}$. This lowest eigenvalue sets the scale of the possible energetic lowering of the ground state due to the introduction of the nonpair part of the interaction. Taking the ratio with the pair-correlated BCS energy of $\Delta^2 N(0)$, we obtain

$$\frac{\tilde{V}}{E_F}\left(\frac{\hbar\omega_{\text{phonon}}}{\Delta}\right)^2\frac{1}{\sqrt{\tilde{N}}}. \tag{3}$$

The ratio scales as $1/\sqrt{\tilde{N}}$ with a prefactor that depends upon material-specific quantities, but can be in the range $\sim 1-10$. Therefore the crossover below which the nonpair correlated interactions become important occurs in a size regime which is typically somewhat smaller than that of the onset of finite size effects due to the coarsening of the electronic energy levels. However, for weakly coupled systems, the influence of the nonpair terms could become significant, depending upon the detailed material- and distance-dependent magnitudes of the nonpair matrix elements. This result is distinct from arguments that relate pairing correlations between non-time-reversed states to the magnetic response of finite-sized superconducting grains[8] in that the current results do not depend on the relative sizes of matrix elements between time-reversed and non-time-reversed states.

This research was supported by National Science Foundation Grants No. DMR-9520554 and DMR-9876232 and by the Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

[1] For example, the pairing correlations embodied by the BCS Hamiltonian (Ref. 9) overpower analogous fourfold correlations (which have similar uniformly signed interaction matrix elements), since the number of many body basis states with fourfold correlation is much smaller than the number with pairwise correlations. Explicitly, an N electron system with $\tilde{N} = 2N(0)\hbar\omega_{\text{phonon}}$ states active in superconductivity has roughly $\binom{\tilde{N}/2}{\tilde{N}/4}$ pair-correlated states in the superposition as compared to only $\binom{\tilde{N}/4}{\tilde{N}/8}$ quartet-correlated states; the quartet correlations then comprise roughly $e^{-\tilde{N}/2}$ times fewer basis states with which to construct the nonpositive submatrix. The simplest correlations afford the largest scope for the accumulation of energetically favorable configurations. (The fraction of nonzero matrix elements in the quartet correlated submatrix does increase slightly, but this increase is insignificant compared to the reduction in the size of the submatrix.)

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[11] The simplest way to see the volume dependence of the matrix elements is to remember that $\lambda = N(0)V$ and λ is independent of system size, whereas $N(0)$ is proportional to volume.

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[13] Variation in the number of contributing many-particle basis states induced by changes in the required correlations is distinct from variations in the number of contributing many-particle basis states induced by changes in the number of electrons. Changing the number of electrons, although it increases the number of contributing basis states factorially, also decreases the fractional number of nonzero matrix elements of the interaction factorially. Increases in the order of the correlation decreases the number of contributing states, but does not cause a similarly sized counteracting increase in the fractional number of nonzero matrix elements.